

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Cracking Heavy Hydrocarbon Oils by means of a Fluidized Bed of Hot Inert-Solid Particles

We, ESSO RESEARCH AND ENGINEERING COMPANY, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to use, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the fluid coking of hydrocarbon oils, particularly heavy low value residual oils. It is more particularly concerned with an improved method of separating the vaporous cracked products therefrom whereby the quality and yield of the products is improved, and the recycle rate of the heavy ends of the cracked products is greatly reduced.

In accordance with the present invention there is provided a process for cracking a heavy hydrocarbon oil in a fluidized bed of finely divided inert solids at an elevated temperature so as to convert the oil to lighter hydrocarbon fractions which are recovered overhead and fractionated, and coke, which is deposited on the inert solids, in which the vapours of the lighter hydrocarbon fractions are scrubbed in a first scrubbing zone with a heavy hydrocarbon fraction to remove entrained solids and hydrocarbon constituents boiling above 1000° F, the vapours from the first scrubbing zone are passed to a second scrubbing zone where they are scrubbed with a lighter scrubbing liquid to remove a heavy gas-oil fraction having an initial boiling-point within the range 800—950° F and a final boiling-point within the range 1000—1100° F and containing compounds that adversely effect cracking catalysts, removing a mixture of scrubbing liquid and condensate from the second scrubbing zone, partially vaporizing without coking the mixture to remove lighter constituents, and recycling the heavy unvaporized residue to the coking zone.

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In some applications it is desirable to pre-heat the feed to the process by having it serve as the above-mentioned heavy oil used in the first scrubbing zone.

When a vacuum tower is used to prepare the fresh feed to the coking zone, it is preferred to recycle the imperfect gas oil fraction to this zone in order to recover its gas oil components free from catalyst contaminants and coke formers. When such facilities are not available, it is preferred to recycle this imperfect gas oil fraction to the uppermost part of the coking bed to vaporize the lighter components with substantially no cracking or coking. The gas oil components are thereby recycled to the scrubbing zone and the coke formers in this fraction are deposited on the contact solids.

The fluid coking process normally consists of a fluid coking vessel and an external heating vessel, e.g., a fluid bed burner. A fluid bed of solids, preferably coke particles produced by the process having a size in the range of about 40—1000 microns, is maintained in the coking zone by the upward passage of a fluidizing gas, e.g., steam. The temperature of the bed is maintained at about 950° F. by circulating solids to the heating vessel and back to the coking bed. The heavy oil to be cracked is injected into the fluid bed and upon contact with the hot solids undergoes pyrolysis evolving lighter hydrocarbon vapors and depositing residue or coke on the solids.

The turbulence of a fluid bed normally results in substantially isothermal conditions and thorough and rapid distribution of the heavy injected oil. Product vapours, after heavy entrained solids are removed, are withdrawn overhead from coking vessel and sent to a scrubber and a fractionator for cooling and separation.

The heavy ends of the product vapours contain high boiling materials that will degrade to coke. The heavy ends also contain a substantial amount of organic salts that are extremely deleterious to cracking catalyst. The fluid coking process is used to upgrade heavy low

value oils to gas oils suitable as catalytic cracking charging stocks. Therefore, the coke formers and catalyst contaminants must be removed from the product.

5 Because the heavy ends separated from the conversion products have a tendency to polymerize and rapidly degrade to coke, the conventional means of fractionating the vapours
10 Instead the vapours are initially contacted and cooled in a scrubbing zone relatively unobstructed with internal devices. The temperature of the liquid collected in the base of the scrubbing zone cannot exceed about 725° F.
15 because it will readily coke at temperatures above this.

In the past it has been the practice to decrease the final endpoint of the gas oil product to a temperature so low as to avoid inclusion
20 of deleterious compounds. This results, however, in the loss of a substantial amount of potential gas oil in the higher boiling bottoms that are recycled to the coking zone.

The coking characteristics of the products
25 prevent the attainment of a sharp separation of the gas oil from the recycled bottoms fraction, i.e. perfect vapour-liquid temperature equilibrium cannot be achieved in the scrubber. Consequently the bottoms fraction contains a
30 substantial amount, up to 30–50%, of gas oil that is of suitable catalytic cracking quality. By recycling this material, the amount of recycle is greatly increased and the repetitious pyrolysis of the gas oil in its passage
35 through the coking zone results in relatively poor product yields and distributions. This problem is further aggravated by the light nature of the recycle bottoms fraction. As it is more volatile
40 than the customary feed to the coking zone, the recycle fraction is customarily injected into the lower portion of the zone so that it will undergo a more severe vapor phase cracking.

In accordance with the present invention,
45 the operation of the coking system is modified to avoid the difficulties of high recycle rates and of poor separation in the scrubbing zone. Instead of condensing only the heavy ends of the coker vapors in the scrubbing zone, two
50 fractions are separated. The highest boiling fraction initially separated from the vapours, which also removes entrained solids, is returned to the coking zone as is customary, but its initial boiling-point is substantially higher,
55 e.g., 1075° F., than that normally obtained in the scrubbing zone, and the fraction is substantially free from gas oil. Thus, this bottoms recycle stream returns the coke particles removed
60 from the vapors to the coking zone as is necessary and only coke formers, and metals, e.g., asphaltenes, are present in this bottoms fraction. A second somewhat lower boiling heavy gas oil is then separated from vapors in the scrubbing zone. This fraction contains some
65 heavier coke-forming material and all of the

contaminants remaining in the vapors after the first bottoms are removed. The vapors are then further processed in a conventional manner. The second gas oil fraction is especially
70 processed to recapture the desirable gas oil components while the undesirable components are returned to the coker and reduced to coke.

Reference to the attached drawings will make this invention clear. Figure 1 depicts a conventional coker with a detached scrubber tower
75 modified in accordance with the teachings of this invention. Figure 2 illustrates another modification of this invention wherein a vacuum tower is used to prepare the feed to the fluid coker and a combination fractionator-scrubber superposed on the coking vessel is
80 used to quench and separate the product vapors.

With particular reference to Figure 1, a
85 customary feed stock, e.g., a residual oil which may be suitably preheated, is injected into a conventional fluid coking vessel 1 via manifold system 2. The injected oil makes contact with a bed of fluidized solids maintained at a coking
90 temperature in a range of about 900° to 1200° F. and undergoes pyrolysis evolving lighter hydrocarbon vapors and depositing coke on the solids. Fluidization gas, e.g., steam is admitted to the base of the vessel by line 4. Solids,
95 after having been stripped of adhering hydrocarbons, are withdrawn from the base of the vessel by line 5 and circulated to an external heating zone. Heated solids are returned to vessel 1 by line 6 to maintain the coking temperature. The vaporous conversion products
100 are withdrawn overhead by line 7 after having entrained solids removed in cyclone system 8.

The vapours are introduced into a scrubber
105 10 where heavy ends and catalyst contaminants are removed. The vapours are initially met with a heavy recycle bottoms fraction supplied by line 11 which serves to condense materials boiling above about 1000° to 1100° F. from the vapors. The scrubbing liquid and the condensed material collect in the base of the
110 scrubber. A portion of this liquid is circulated by line 12 and cooled in heat exchanger 13 to supply the heavy scrubbing oil. The remainder is recycled by line 16 to the lower portion
115 of the coking zone.

The vapours then pass upwardly through the scrubbing tower 10 past a drawoff plate 17
120 and are contacted with a lighter scrubbing oil supplied by line 18. This lighter oil serves to condense from the vapours material boiling above about 800° to 950° F. The lighter fraction absorbs substantially all of the catalyst contaminants in the vapours and also substantial amounts of catalytic cracking quality gas oils. The vapours
125 are then removed from the top of the scrubber by line 19 and sent to further recovery equipment, e.g., a fractionator.

The lighter fraction condensed in the scrubber is withdrawn from drawoff plate 17 by line
130

20 and a portion of it is passed through heat exchanger 21 to supply the lighter scrubbing oil. The remainder is circulated by line 20 to the uppermost portion of the fluid bed and injected into it. In this manner the lighter constituents of this fraction are only vaporized and are not subjected to coking or cracking, while the heavy constituents are deposited on the solids to be subjected to liquid phase coking. If this fraction contains predominant proportions of gas oils then it may be injected higher up into the coker in the disperse solids phase or into the cyclone inlet which will further avoid pyrolysis of the gas oil. The solids entrained in the vapours will supply sufficient surface for any material that may condense.

In modifications of the invention it may be desired to process the imperfect gas oil in line 20 by other suitable means. For example, this fraction may be mildly vaporized in an external vaporization zone, such as a fluidized bed or a transfer line zone, by contact with particulate solids maintained at a temperature somewhat lower than the coking temperature, e.g., 600–800° F. The vapours produced by this procedure can be returned directly to the second scrubbing zone while the solids in the secondary zone that contain the liquid deposit can be returned to coking zone, whereby the liquid on the solids is completely vaporized and coked.

EXAMPLE.

A fluid coker operating at a temperature of 950° F. using particulate coke produced by the process having a size in the range of 40–800 microns, has injected into it a residual oil having a Conradson carbon of 24 wt. %, API gravity of 4.2°, and an initial boiling point of 1000° F. 10 wt. % steam based on feed is injected into the base of the coker as fluidizing gas. 10 pounds of heated solids/lb. of feed are injected into the coker at a temperature of 1125° F. and an equivalent amount of solids is withdrawn from the base of the coker and circulated to a heating zone. Under these conditions about 75wt. % of the feed is converted to products boiling below 1000° F.

The vapours so produced are introduced into the lower portion of a scrubbing tower where they make contact with a recycle bottoms fraction that has an initial boiling-point of 1075° F and an inlet temperature of 600° F. in amounts sufficient to condense 20 vol. % of the vapours or all material boiling above 1030° F. The material so condensed is recycled in the coking zone at a rate of 25 vol./vol. of fresh feed. The vapours are next scrubbed with a recycled heavy gas oil boiling within the range 800–950° F and having an inlet temperature of 500° F. supplied in amounts sufficient to condense about 10 vol. % of the remaining vapours or all material boiling above 950° F. The vapours are then re-

moved as product. Part of the heavy gas oil fraction condensed is recycled to the scrubber and another part is injected onto the surface of the coking bed at a rate of 15 vol./vol. of fresh feed.

Figure 2 serves to illustrate an embodiment of this invention, preferred when vacuum distillation facilities are available. Illustrated is a fluid coking vessel 50 with a superposed scrubber-fractionator 51 and a vacuum distillation tower 52. The feed to the process is introduced into the vacuum tower 52 by line 53 and may comprise, for example, atmospheric residuum obtained by the atmospheric fractionation of a whole crude. Gas oils boiling up to about 1000° F. are separated from the residuum and removed from the tower by line 54. The remaining bottoms or vacuum residuum is transferred and injected into the coking vessel by line 55.

The vapours produced by the coking reaction pass overhead through cyclone 56 wherein entrained solids are removed, and are introduced into the base of the scrubber-fractionator. The scrubber-fractionator has disc-and-doughnut baffles 57 in the lower portion to promote effective contact between the liquid and vapours, and conventional fractionation trays or plates 58 in the upper portion. The vapours are initially contacted with a heavy scrubbing oil sprayed into the scrubbing section by line 59. As previously noted this heavy scrubbing oil can comprise a portion or all of the vacuum feed to the coking zone. Thus some of the vacuum residuum in line 55 may be transferred to line 59 and there introduced into the scrubbing tower. The material initially condensed from the vapors is removed by line 60. A portion of it is cooled in heat exchanger 61 to form a scrubbing oil. The remainder is recycled to the coking zone by line 62. The vapours then passed up into the upper part of the scrubbing zone and are met with a lighter scrubbing oil supplied by line 63. The material condensed in this manner collects on drawoff plate 64 and is removed by line 65. A portion of this lighter material is cooled in heat exchanger 66 and returned as the lighter scrubbing oil.

The vapours then pass to the upper part of the scrubber-fractionator and are separated by conventional means into the various product fractions desired. For example, a heavy gas oil may be separated and removed by line 67, a heating oil by line 68, a naphtha or gasoline fraction by line 69, and light gases by line 70. It is preferred to cool a portion of the gas oil product in heat exchanger 71 and introduce it into the tower via line 72 at a point just below the fractionation section in order to ensure that all heavy ends and catalyst contaminants are removed from the vapors.

According to a subsidiary feature of this invention, the contents of line 65, i.e., the lighter fractions separated in the second scrub-

bing zone, are transferred and introduced into the vacuum tower 52 to recover the gas oil components. The heavier components of this fraction then are removed from the vacuum tower along with the vacuum residuum in line 55. In this manner a clean gas oil of good catalytic cracking quality is obtained from the coker vapors in the scrubber-fractionator and yet the gas oils necessarily condensed in the scrubbing zone are not needlessly thermally degraded by repetitious passage through the coking zone. This does not appreciably reduce the capacity of unit 52 because of the relatively low volume of the lighter fractions.

While it is customary to operate a fluid coker to obtain complete elimination of the charge introduced into the coking zone, in some cases it is desirable to take a residual oil product. For the process illustrated in Figure 2 a portion of the heavy bottoms in line 62 normally recycled to the coker, may be withdrawn by line 73 as a residual oil product.

WHAT WE CLAIM IS:—

1. A process for cracking a heavy hydrocarbon oil in a fluidized bed of finely divided inert solids at an elevated temperature so as to convert the oil to lighter hydrocarbon fractions, which are recovered overhead and fractionated, and coke, which is deposited on the inert solids, in which the vapours of the lighter hydrocarbon fractions are scrubbed in a first scrubbing zone with a heavy hydrocarbon fraction to remove entrained solids and hydrocarbon constituents boiling above 1000° F, the vapours from the first scrubbing zone are passed to a second scrubbing zone where they are scrubbed with a lighter scrubbing liquid to remove a heavy gas-oil fraction having an initial boiling-point within the range 800—950° F and a final boiling point within the range 1000—1100° F. and containing compounds that adversely effect cracking catalysts, removing a mixture of scrubbing liquid and condensate from the second scrubbing zone, partially vaporizing without coking the mixture to remove lighter constituents, and recycling the heavy unvaporized residue to the coking zone.

2. A process as claimed in claim 1 in which the mixture of scrubbing fluid and condensate obtained from the second scrubbing zone is brought into contact with a hot fluidized solid bed to vaporize the lighter constituents comprising the gas oil and the heavier constituents are deposited on the solids and are removed with the solids and transferred to the coking zone.

3. A process as claimed in claim 1 or 2 in which the mixture of scrubbing liquid and condensate from the second scrubbing zone is passed to the upper part of the fluidized bed

whereby the lighter constituents are carried off together with the product vapours and treated with them, and the heavier constituents are deposited upon the fluidized solid and subjected to liquid-phase coking.

4. A process as claimed in Claim 1 in which the feed to the coking zone comprises the bottoms residue of a vacuum still and in which the mixture of scrubbing liquid and condensate from the second scrubbing zone is recycled to the vacuum still whereby the lighter constituents are removed overhead with the other light constituents from the vacuum distillation and the heavier constituents are collected in the bottom of the vacuum still together with the distillation bottoms and the mixture is recycled to the coking zone.

5. A process as claimed in Claim 1 or 2 in which the scrubbing liquid fed to the first scrubbing zone is part or all of the mixture of scrubbing liquid and condensate removed from the said zone.

6. A process as claimed in Claim 5 in which the scrubbing liquid is cooled by heat exchange before being passed to the first scrubbing zone.

7. A process as claimed in any one of Claims 1—6 in which the initial scrubbing material used in the first scrubbing zone is part or all of the feed to the coking zone.

8. A process as claimed in any one of Claims 1—6 in which the scrubbing liquid used in the second scrubbing zone is the mixture of scrubbing liquid and condensate removed from that zone.

9. A process as claimed in Claim 8 in which the said mixture is cooled by heat exchange before being recycled to the second scrubbing zone.

10. A process as claimed in any one of Claims 1—9 in which the vapours leaving the second scrubbing zone are scrubbed with the heaviest gas-oil fractionation product before passing to the fractionation zone.

11. A process as claimed in any one of Claims 1—10, in which the first and second scrubbing zones are arranged in vertical juxtaposition with each other together with a superposed fractionating zone in a single vessel arranged vertically above and in juxtaposition to the said coking vessel.

12. A process as claimed in Claim 1, when carried out substantially as described in the foregoing example.

13. A process as claimed in Claim 1, when carried out in apparatus substantially as described with reference to Fig. 1 or Fig. 2 of the accompanying drawing.

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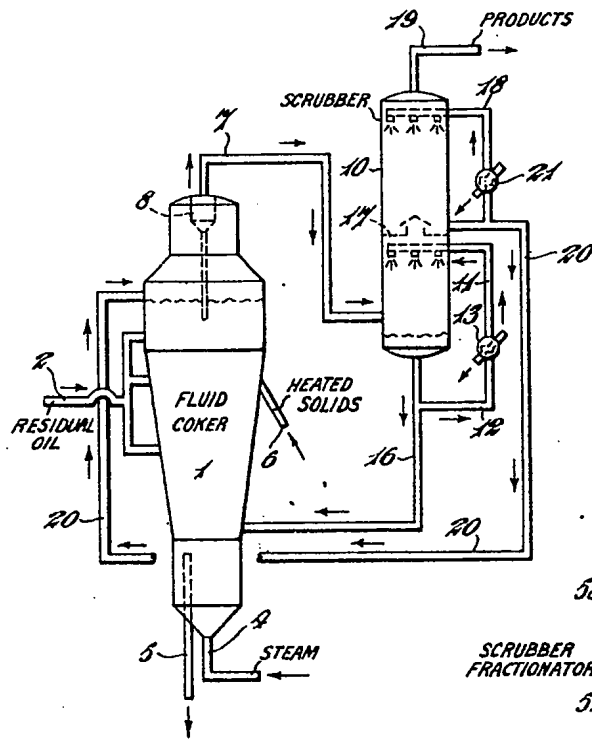


Fig. 1.

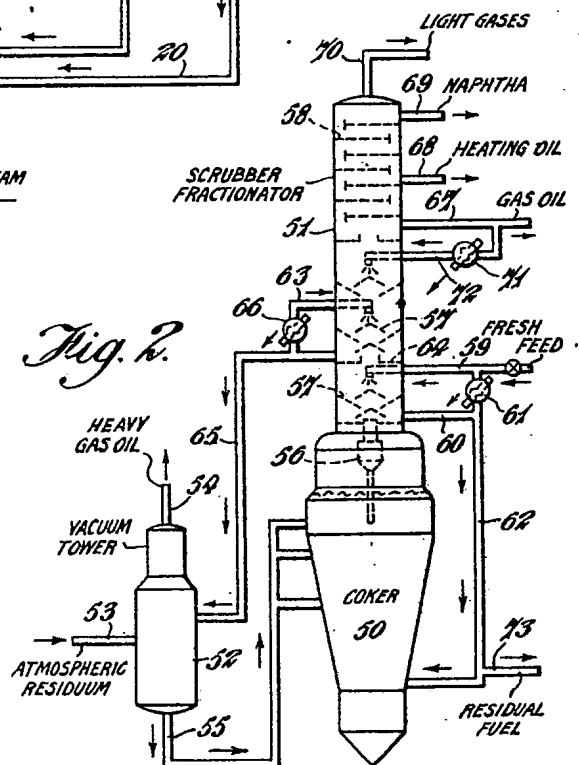


Fig. 2.